

Identities for density functionals linking functionals of different densities.

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In electron density functional theory formal properties of density functionals play an important role in constructing and testing approximate functionals. In this paper it is shown that the equation

$$G^\gamma[\rho_N] - G^\gamma[\rho_{N-1}^\gamma] = \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \frac{\delta G^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})}$$

is satisfied by a number of functionals that are of interest in density functional theory. In particular it is satisfied by $E_{hxc}^\gamma[\rho]$, the sum of the Hartree and exchange-correlation energies. The parameter γ scales the mutual electron Coulomb interaction energy while $\rho_N(\mathbf{r})$ and $\rho_{N-1}^\gamma(\mathbf{r})$ are N -electron and $(N-1)$ -electron densities determined from the same adiabatic scaled external potential of the N -electron system at coupling strength γ .

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I. INTRODUCTION

The Kohn-Sham (KS) formulation¹ of Density Functional Theory (DFT)² is one of the most important tools for the calculation of electronic structure of molecules and solids. In all practical applications of DFT, however, approximations to the exact functionals have to be made³⁻⁷. Exact relations for density functionals and density functional derivatives can play an important role in the development of accurate approximations to the exact functionals. A successful approach to the design of improved approximate density functionals is by 'constraint satisfaction'⁸, where the approximate functionals are required to satisfy properties of the exact functionals. With this in mind, the following relations for DFT energy functionals are derived:

$$\begin{aligned} & F^\gamma[\rho_N] - F^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \frac{\delta F^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})} \end{aligned} \quad (1)$$

$$\begin{aligned} & V_{ee}^\gamma[\rho_N] - V_{ee}^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \frac{\delta V_{ee}^\gamma[\rho_N]}{\delta \rho_N^1(\mathbf{r})} \end{aligned} \quad (2)$$

$$\begin{aligned} & T^\gamma[\rho_N] - T^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \frac{\delta T^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})} \end{aligned} \quad (3)$$

$$\begin{aligned} & T_c^\gamma[\rho_N] - T_c^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta T_c^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})}. \end{aligned} \quad (4)$$

$$\begin{aligned} & T^0[\rho_N] - T^0[\rho_{N-1}^\gamma] \\ &= \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta T^0[\rho_N]}{\delta \rho_N(\mathbf{r})}. \end{aligned} \quad (5)$$

$$\begin{aligned} & E_{hxc}^\gamma[\rho_N] - E_{hxc}^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta E_{hxc}^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})}. \end{aligned} \quad (6)$$

Here ρ_N and ρ_{N-1}^γ are the ground state charge densities of an interacting N and $(N-1)$ electron system with the same single particle multiplicative external potential $v_{\text{ext}}^\gamma([\rho_N])$.

The potential $v_{\text{ext}}^\gamma([\rho_N])$ is constructed to keep the charge density of the N electron system independent of the coupling strength parameter γ^{9-12} that scales the electron-electron interaction strength. At $\gamma = 1$ full strength Coulomb interaction between electrons is included and the external potential $v_{\text{ext}}^\gamma([\rho_N])$ is the external potential of the fully interacting system, while $\gamma = 0$ corresponds to the non-interacting Kohn-Sham potential. $F^\gamma[\rho]$ is the sum of the kinetic energy functional $T^\gamma[\rho]$ and the mutual Coulomb interaction energy $\gamma V_{ee}^\gamma[\rho]$ at interaction strength γ and density ρ . $T_c^\gamma[\rho]$ is the correlation part of the kinetic energy and $E_{hxc}^\gamma[\rho]$ is the sum of the Hartree and exchange-correlation energy.

As corollaries recursion relations are satisfied. For $G^\gamma[\rho] = F^\gamma[\rho]$, $T^\gamma[\rho]$, $V_{ee}^\gamma[\rho]$, $T_c^\gamma[\rho]$, $T^0[\rho]$ or $E_{hxc}^\gamma[\rho]$,

$$G^\gamma[\rho_N] - G^\gamma[\rho_{N-M}^\gamma] = \sum_{L=0}^{M-1} \int d^3r (\rho_{N-L}^\gamma(\mathbf{r}) - \rho_{N-1-L}^\gamma(\mathbf{r})) \frac{\delta G^\gamma[\rho_{N-L}^\gamma]}{\delta \rho_{N-L}^\gamma(\mathbf{r})}, \quad M \leq N-1. \quad (7)$$

Here the densities $\rho_{N-L}^\gamma(\mathbf{r})$ are the $(N-L)$ -particle densities derived from the groundstate wavefunctions of $(N-L)$ -particle Hamiltonians with mutual Coulomb interaction $\gamma \hat{V}_{ee}$ and external potential $v_{\text{ext}}^\gamma([\rho_N])$. For $G^\gamma[\rho] = V_{ee}^\gamma[\rho_N]$, $T_c^\gamma[\rho_N]$ or $E_{hxc}^\gamma[\rho_N]$, $G^\gamma[\rho_1^\gamma] = 0$ and the functionals can be written as

$$G^\gamma[\rho_N] = \sum_{L=0}^{N-2} \int d^3r (\rho_{N-L}^\gamma(\mathbf{r}) - \rho_{N-1-L}^\gamma(\mathbf{r})) \frac{\delta G^\gamma[\rho_{N-L}^\gamma]}{\delta \rho_{N-L}^\gamma(\mathbf{r})}. \quad (8)$$

These identities relate functionals at different particle numbers and are likely to place stringent restrictions on the possible forms that potential approximate functionals can assume.

II. PROOF OF EQUATIONS 1-3

In the adiabatic connection approach⁹⁻¹² of the constrained minimization formulation of density functional theory^{1,2,13,14} the Hamiltonian \hat{H}^γ for a system of N electrons is given by

$$\hat{H}^\gamma = \hat{T} + \gamma \hat{V}_{ee} + \hat{v}_{N,\text{ext}}^\gamma[\rho_N]. \quad (9)$$

Atomic units, $\hbar = e = m = 1$ are used throughout. \hat{T} is the kinetic energy operator,

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \quad (10)$$

and $\gamma\hat{V}_{ee}$ is a scaled electron-electron interaction,

$$\gamma\hat{V}_{ee} = \gamma \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (11)$$

The external potential

$$\hat{v}_{\text{ext}}^\gamma[\rho_N] = \sum_{i=1}^N v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}_i), \quad (12)$$

is constructed to keep the charge density fixed at $\rho_N(\mathbf{r})$, the ground state charge density of the fully interacting system ($\gamma = 1$), for all values of the coupling constant γ . The external potential has the form^{14,15}

$$\begin{aligned} v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}) &= (1 - \gamma) v_{hx}([\rho_N]; \mathbf{r}) \\ &+ v_c^1([\rho_N]; \mathbf{r}) - v_c^\gamma([\rho_N]; \mathbf{r}) + v_{\text{ext}}^1([\rho_N]; \mathbf{r}), \end{aligned} \quad (13)$$

where $v_{\text{ext}}^1([\rho_N]; \mathbf{r}) = v_{\text{ext}}(\mathbf{r})$ is the external potential at full coupling strength, $\gamma = 1$, and $v_{\text{ext}}^0([\rho_N]; \mathbf{r})$ is the non-interacting Kohn-Sham potential. The exchange plus Hartree potential^{16,17} $v_{hx}([\rho_N]; \mathbf{r})$, is independent of γ , while the correlation potential $v_c^\gamma([\rho_N]; \mathbf{r})$ depends in the scaling parameter γ .

The chemical potential

$$\mu = E_N^\gamma(v_{\text{ext}}^\gamma[\rho]) - E_{N-1}^\gamma(v_{\text{ext}}^\gamma[\rho]) \quad (14)$$

depends on the asymptotic decay of the charge density^{16–18}, and hence is independent of the coupling constant γ ^{19,20}. In Eq. (14) E_{N-1}^γ is the groundstate energy of the $(N - 1)$ -electron system with the same single-particle external potential $v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r})$ as the N -electron system:

$$\begin{aligned} \hat{H}^\gamma \left| \Psi_{\rho_M^\gamma}^\gamma \right\rangle &= E_M^\gamma \left| \Psi_{\rho_M^\gamma}^\gamma \right\rangle \\ \hat{H}^\gamma &= \hat{T} + \gamma\hat{V}_{ee} + \hat{v}_{M,\text{ext}}^\gamma[\rho_N] \\ \hat{v}_{M,\text{ext}}^\gamma[\rho_N] &= \sum_{i=1}^M v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}_i) \end{aligned} \quad (15)$$

Note that by construction of $v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r})$, Eq. (13), $\rho_N = \rho_N^1$ is independent of γ , but the groundstate density of the $(N - 1)$ -electron system derived from the same external potential at coupling strength γ , ρ_{N-1}^γ , will in general be a function of γ .

Define the energy functional^{13,16,17}

$$\begin{aligned} F^\gamma[\rho] &= \left\langle \Psi_\rho^\gamma \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi_\rho^\gamma \right\rangle \\ &= \min_{\Psi \rightarrow \rho} \left\langle \Psi \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi \right\rangle. \end{aligned} \quad (16)$$

According to the Levy constrained minimization formulation¹³, the wavefunction $|\Psi_\rho^\gamma\rangle$ yields the density ρ and minimizes $\left\langle \Psi \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi \right\rangle$. $F^\gamma[\rho]$ can be decomposed as^{16,17}

$$F^\gamma[\rho] = T^0[\rho] + \gamma E_{hx}[\rho] + E_c^\gamma[\rho], \quad (17)$$

The correlation energy $E_c^\gamma[\rho]$ is defined as¹⁴

$$\begin{aligned} E_c^\gamma[\rho] &= \left\langle \Psi_\rho^\gamma \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi_\rho^\gamma \right\rangle \\ &\quad - \left\langle \Psi_\rho^0 \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi_\rho^0 \right\rangle, \end{aligned} \quad (18)$$

where $|\Psi_\rho^0\rangle$ is the Kohn-Sham independent particle groundstate wavefunction that yields the same density as the interacting system at coupling strength γ . $E_{hx}[\rho]$ is the sum of the Hartree and exchange energy

$$E_{hx}[\rho] = \left\langle \Psi_\rho^0 \left| \hat{V}_{ee} \right| \Psi_\rho^0 \right\rangle \quad (19)$$

and the kinetic energy functional $T^0[\rho]$ is given by.

$$T^0[\rho] = \left\langle \Psi_\rho^0 \left| \hat{T} \right| \Psi_\rho^0 \right\rangle. \quad (20)$$

The full kinetic energy

$$\begin{aligned} T^\gamma[\rho] &= \left\langle \Psi_\rho^\gamma \left| \hat{T} \right| \Psi_\rho^\gamma \right\rangle \\ &= T^0[\rho] + T_c^\gamma[\rho], \end{aligned} \quad (21)$$

with the correlation part of the kinetic energy defined as

$$T_c^\gamma[\rho] = \left\langle \Psi_\rho^\gamma \left| \hat{T} \right| \Psi_\rho^\gamma \right\rangle - \left\langle \Psi_\rho^0 \left| \hat{T} \right| \Psi_\rho^0 \right\rangle. \quad (22)$$

Assuming that $F^\gamma[\rho]$ is defined for non-integer electrons^{16,17,21}, at the solution point

$$\frac{\delta F^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})} + v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}) = \mu \quad (23)$$

Note that by definition of $F^\gamma[\rho]$

$$\begin{aligned} E_N^\gamma(v_{\text{ext}}^\gamma[\rho_N]) &= F^\gamma[\rho_N] + \int d^3r \rho_N(\mathbf{r}) v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}) \\ E_{N-1}^\gamma(v_{\text{ext}}^\gamma[\rho_N]) &= F^\gamma[\rho_{N-1}^\gamma] + \int d^3r \rho_{N-1}^\gamma(\mathbf{r}) v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}). \end{aligned} \quad (24)$$

From (14) and (24),

$$F^\gamma[\rho_N] - F^\gamma[\rho_{N-1}^\gamma] = \mu - \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}). \quad (25)$$

Since

$$\int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) = 1, \quad (26)$$

it follows from (23), (25) and (26) that

$$F^\gamma[\rho_N] - F^\gamma[\rho_{N-1}^\gamma] = \int d^3r (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \frac{\delta F^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})}. \quad (27)$$

In a recent paper, starting from the virial theorem for the interacting system²², the author showed that

$$\begin{aligned} & V_{ee}^\gamma[\rho_N^1] - V_{ee}^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r \frac{\delta V_{ee}^\gamma[\rho_N^1]}{\delta \rho_N^1(\mathbf{r})} (\rho_N^1(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})). \end{aligned} \quad (28)$$

Combining (27) and (28) yields

$$\begin{aligned} & T^\gamma[\rho_N] - T^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r \frac{\delta T^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})} (\rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})). \end{aligned} \quad (29)$$

III. PROOF OF EQUATIONS 4-6

The mutual electron-electron repulsion energy functional can be expressed as

$$V_{ee}^\gamma[\rho_N^\gamma] = E_{hx}[\rho] + \frac{E_c^\gamma[\rho] - T_c^\gamma[\rho]}{\gamma}, \quad (30)$$

which follows from Eq. (18) and the definitions (17) and (21)^{16,17}. Substitute Eq. (30) in Eq. (28), take the derivative with respect to γ :

$$\begin{aligned} & \frac{d}{d\gamma} \frac{1}{\gamma} ((E_c^\gamma[\rho_N] - T_c^\gamma[\rho_N]) - (E_c^\gamma[\rho_{N-1}^\gamma] - T_c^\gamma[\rho_{N-1}^\gamma])) \\ & - \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} v_{hx}([\rho_{N-1}^\gamma]; \mathbf{r}) \\ &= -\frac{1}{\gamma} \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} (\gamma v_{hx}([\rho_N]; \mathbf{r}) + v_c([\rho_N]; \mathbf{r})) \\ & + \frac{1}{\gamma} \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} \frac{\delta T_c^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})} \\ & + \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{d}{d\gamma} \frac{1}{\gamma} \frac{\delta}{\delta \rho_N(\mathbf{r})} (E_c^\gamma[\rho_N] - T_c^\gamma[\rho_N]). \end{aligned} \quad (31)$$

It follows from the definition of $E_c^\gamma[\rho_N]$, Eq. (18) that¹⁴

$$\frac{\partial}{\partial \gamma} E_c^\gamma[\rho_N] = \frac{1}{\gamma} (E_c^\gamma[\rho_N] - T_c^\gamma[\rho_N]). \quad (32)$$

With the aid of Eqs. (31), (A10) and (32), it can be shown that

$$\begin{aligned} & \frac{d}{d\gamma} (T_c^\gamma[\rho_N]) - T_c^\gamma[\rho_{N-1}^\gamma] \\ &= \frac{d}{d\gamma} \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta T_c^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})}. \end{aligned} \quad (33)$$

Integrating with respect to γ and taking into account that $T_c^0[\rho] = 0$ (see Eq. (22)), it follows that

$$\begin{aligned} & T_c^\gamma[\rho_N] - T_c^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta T_c^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})}. \end{aligned} \quad (34)$$

As a consequence, from Eqs. (29) and (34)

$$\begin{aligned} & T^0[\rho_N] - T^0[\rho_{N-1}^\gamma] \\ &= \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta T^0[\rho_N]}{\delta \rho_N(\mathbf{r})}. \end{aligned} \quad (35)$$

With

$$E_{hxc}^\gamma[\rho] = \gamma E_{hx}[\rho] + E_c^\gamma[\rho] \quad (36)$$

it follows from Eqs. (28), (30) and (34) that

$$\begin{aligned} & E_{hxc}^\gamma[\rho_N] - E_{hxc}^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta}{\delta \rho_N(\mathbf{r})} E_{hxc}^\gamma[\rho_N]. \end{aligned} \quad (37)$$

IV. PROOF OF RECURSION RELATIONS, EQUATION 7

The identities in Eqs. (1) to (6) all have the form

$$\begin{aligned} & G^\gamma[\rho_N] - G^\gamma[\rho_{N-1}^\gamma] \\ &= \int d^3r' (\rho_N(\mathbf{r}') - \rho_{N-1}^\gamma(\mathbf{r}')) \frac{\delta}{\delta \rho_N(\mathbf{r})} G^\gamma[\rho_N]. \end{aligned} \quad (38)$$

These identities were derived with $\gamma = 1$, full interaction strength, as the starting point. The arguments used before are equally applicable when the Coulomb operator $\gamma \hat{V}_{ee}$ is replaced by $\beta \gamma \hat{V}_{ee}$, the coupling strength is scaled by β and the external potential at full coupling strength $\chi = 1$, is taken as $v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}_i)$. Here β plays the role that γ played before. Recursion relations can now be derived at coupling strength γ . If the single particle external potential is kept fixed, i.e. for an M -electron system

$$\hat{v}_{\text{ext}}^{M,\gamma}[\rho_N] = \sum_{i=1}^M v_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}_i) \quad (39)$$

and $\rho_M^{\beta=1} \equiv \rho_M^\gamma(v_{\text{ext}}^\gamma[\rho_N])$ is the M -electron density constructed from a groundstate of the M -electron Hamiltonian $\hat{H}_M^{\beta=1} = \hat{T} + \gamma \hat{V}_{ee} + \hat{v}_{\text{ext}}^{M,\gamma}[\rho_N]$. Thus, from Eq. (38), but starting from ρ_{N-1}^γ ,

$$\begin{aligned} & G^\gamma[\rho_{N-1}^\gamma] - G^\gamma[\rho_{N-2}^\gamma] \\ &= \int d^3r (\rho_{N-1}^\gamma(\mathbf{r}) - \rho_{N-2}^\gamma(\mathbf{r})) \frac{\delta G^\gamma[\rho_{N-1}^\gamma]}{\delta \rho_{N-1}^\gamma(\mathbf{r})}. \end{aligned} \quad (40)$$

Continuing this pattern leads to

$$\begin{aligned} & G^\gamma[\rho_N] - G^\gamma[\rho_{N-M}^\gamma] \\ &= \sum_{L=0}^{M-1} \int d^3r (\rho_{N-L}^\gamma(\mathbf{r}) - \rho_{N-1-L}^\gamma(\mathbf{r})) \frac{\delta G^\gamma[\rho_{N-L}^\gamma]}{\delta \rho_{N-L}^\gamma(\mathbf{r})}, \quad M \leq N-1. \end{aligned} \quad (41)$$

For $G^\gamma[\rho_N] = V_{ee}^\gamma[\rho_N]$, $T_c^\gamma[\rho_N]$ or $E_{hxc}^\gamma[\rho_N]$, $G^\gamma[\rho_1^\gamma] = 0$, hence for $V_{ee}^\gamma[\rho_N]$, $T_c^\gamma[\rho_N]$ and $E_{hxc}^\gamma[\rho_N]$

$$G^\gamma[\rho_N] = \sum_{L=0}^{N-2} \int d^3r (\rho_{N-L}^\gamma(\mathbf{r}) - \rho_{N-1-L}^\gamma(\mathbf{r})) \frac{\delta G^\gamma[\rho_{N-L}^\gamma]}{\delta \rho_{N-L}^\gamma(\mathbf{r})}. \quad (42)$$

V. DISCUSSION AND SUMMARY

The identities reported here were derived by reference to the eigenfunctions of many particle Hamiltonians, though indirectly, via Eq. (23). They therefore are valid for w -representable densities^{16,17}, in other words for densities that can be determined from ground-state wavefunctions of a many-particle Hamiltonian. The assumption was made that all functional derivatives are well behaved and this implies that the functionals are defined for non-integer particle numbers²¹. In the derivations no explicitly reference was made to the

structure of the wavefunctions or density, the equations are therefore valid for all groundstate densities. Specifically they are valid for all degenerate densities.

Equation (6) may be the most useful of the set presented here for testing approximate exchange correlation functionals. The obvious test can be done at full coupling strength, where for a real system the external potential is the Coulomb interaction with the nuclei, and requires two separate self-consistent Kohn-Sham calculations for the N and $(N - 1)$ electron systems to determine $\rho_N^1(\mathbf{r})$ and $\rho_{N-1}^1(\mathbf{r})$. For $T^0[\rho]$ a single Kohn-Sham calculation is sufficient. The other identities are more difficult to use for testing purposes since they are satisfied by the functionals of the exact densities which will require independent calculations to determine accurate densities.

If the functionals can be expanded as a series in the usual form¹⁶

$$G^\gamma[\rho] = G^\gamma[\rho_0] + \sum_{n=1}^{\infty} \frac{1}{n!} \int d^3r_1 \dots d^3r_n (\rho(\mathbf{r}_1) - \rho_0(\mathbf{r}_1)) \dots (\rho(\mathbf{r}_n) - \rho_0(\mathbf{r}_n)) \frac{\delta^n G^\gamma[\rho_0]}{\delta \rho(\mathbf{r}_1) \dots \delta \rho(\mathbf{r}_n)} \quad (43)$$

then (38) implies that

$$0 = \sum_{n=2}^{\infty} \frac{1}{n!} \int d^3r_1 \dots d^3r_n (\rho_N(\mathbf{r}_1) - \rho_{N-1}^\gamma(\mathbf{r}_1)) \dots (\rho_N(\mathbf{r}_n) - \rho_{N-1}^\gamma(\mathbf{r}_n)) \frac{\delta^n G^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r}_1) \dots \delta \rho_N(\mathbf{r}_n)}, \quad (44)$$

for $F^\gamma[\rho]$, $T^\gamma[\rho]$, $V_{ee}^\gamma[\rho]$, $T_c^\gamma[\rho]$, $T^0[\rho]$ and $E_{hxc}^\gamma[\rho]$. Equation (44) in itself places a constraint on the structure of potential approximate density functionals.

Note that for $\gamma = 0$,

$$\rho_{N-L}^0(\mathbf{r}) - \rho_{N-1-L}^0(\mathbf{r}) = |\phi_{N-L}(\mathbf{r})|^2 \quad (45)$$

where $\phi_i(\mathbf{r})$ is an eigenfunction of the Kohn-Sham Hamiltonian with corresponding eigenvalue ε_i ordered so that $\varepsilon_i \leq \varepsilon_{i+1}$. Equation (42), for $\gamma = 0$, becomes

$$G^\gamma[\rho_N] = \sum_{L=0}^{N-2} \int d^3r |\phi_{N-L}(\mathbf{r})|^2 \frac{\delta G^\gamma \left[\sum_{i=1}^{N-L} |\phi_i(\mathbf{r})|^2 \right]}{\delta \rho_{N-L}^0(\mathbf{r})}, \quad (46)$$

and $\rho_{N-L}^0(\mathbf{r}) = \sum_{i=1}^{N-L} |\phi_i(\mathbf{r})|^2$. Eq. (42) is valid for $G^\gamma[\rho_N] = E_{hxc}^\gamma[\rho_N]$ and for $G^\gamma[\rho_N] = \frac{1}{\gamma} E_{hxc}^\gamma[\rho_N]$ and since $\lim_{\gamma \rightarrow 0} \frac{1}{\gamma} E_c^\gamma[\rho_N] = 0$ ¹⁴, it follows from (36) that

$$E_{hx}[\rho_N] = \sum_{L=0}^{N-2} \int d^3r |\phi_{N-L}(\mathbf{r})|^2 v_{hx} \left[\sum_{i=1}^{N-L} |\phi_i(\mathbf{r})|^2 \right]. \quad (47)$$

From the definition of the Hartree potential,

$$v_h([\rho]; \mathbf{r}) = \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

it follows from Eq. (6) and (36) that

$$\begin{aligned} & E_x[\rho_N] - E_x[\rho_{N-1}^0] \\ &= \int d^3r v_x([\rho_N]; \mathbf{r}) |\phi_N(\mathbf{r})|^2 \\ &+ \frac{1}{2} \int d^3r d^3r' |\phi_N(\mathbf{r})|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\phi_N(\mathbf{r}')|^2. \end{aligned} \quad (48)$$

Eqs. (47) and (48) were discovered by Levy and Görling some time ago.²³

The only other identity that survives at $\gamma = 0$ is the independent particle Kohn-Sham kinetic energy:

$$\begin{aligned} & T^0[\rho_N] - T^0[\rho_{N-1}^0] \\ &= \int d^3r \frac{\delta T^0[\rho_N]}{\delta \rho_N(\mathbf{r})} |\phi_N(\mathbf{r})|^2. \end{aligned} \quad (49)$$

This expression follows trivially from the Kohn-Sham expression for the independent particle kinetic energy. All identities are valid at $\gamma \neq 0$.

In summary, equations that a set of exact density functionals satisfy for functionals of different densities, where the densities are derived from the same external potential, were derived. As a corollary, it was shown that the functionals can be expressed as a sum over integrals of functional derivatives, where the sum runs over all w -representable densities for the same external potential that integrate to an integer less than the particle number. These relations place stringent constraints on functionals that appear in density functional theory and it will be difficult to satisfy by approximate functionals.

Appendix A

From Eq. (18)

$$\begin{aligned} & \frac{E_c^\gamma[\rho_{N-1}^\gamma] - T_c^\gamma[\rho_{N-1}^\gamma]}{\gamma} \\ &= \left\langle \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{V}_{ee}^\gamma \right| \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle - \left\langle \Psi_{\rho_{N-1}^0}^0 \left| \hat{V}_{ee} \right| \Psi_{\rho_{N-1}^0}^0 \right\rangle. \end{aligned} \quad (A1)$$

The derivative of $E_c^\gamma [\rho_{N-1}^\gamma]$ with respect to γ , from definition (18), can therefore be expressed as

$$\begin{aligned}
& \frac{\partial}{\partial \gamma} E_c^\gamma [\rho_{N-1}^\gamma] \\
&= \frac{E_c^\gamma [\rho_{N-1}^\gamma] - T_c^\gamma [\rho_{N-1}^\gamma]}{\gamma} \\
&+ \left\langle \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle \\
&+ \left\langle \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{T} + \gamma \hat{V}_{ee} \right| \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle \\
&- \left\langle \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^0 \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi_{\rho_{N-1}^\gamma}^0 \right\rangle \\
&- \left\langle \Psi_{\rho_{N-1}^\gamma}^0 \left| \hat{T} + \gamma \hat{V}_{ee} \right| \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^0 \right\rangle. \tag{A2}
\end{aligned}$$

Upon adding and subtracting (c.c. stands for the complex conjugate of the previous term)

$$\begin{aligned}
& \left(\left\langle \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{v}_{N-1, \text{ext}}^\gamma [\rho_N] \right| \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle + \text{c.c.} \right) \\
&+ \left(\left\langle \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{v}_{N-1, \text{ext}}^0 [\rho_N] \right| \Psi_{\rho_{N-1}^\gamma}^0 \right\rangle + \text{c.c.} \right) \tag{A3}
\end{aligned}$$

and utilizing the normalization of the wavefunctions which implies that

$$\frac{\partial}{\partial \gamma} \left\langle \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle = 0, \tag{A4}$$

Eq. (22) becomes

$$\begin{aligned}
& \frac{\partial}{\partial \gamma} E_c^\gamma [\rho_{N-1}^\gamma] \\
&= \frac{E_c^\gamma [\rho_{N-1}^\gamma] - T_c^\gamma [\rho_{N-1}^\gamma]}{\gamma} \\
&- \left\langle \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{v}_{\text{ext}}^\gamma [\rho_N] \right| \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle - \left\langle \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{v}_{\text{ext}}^\gamma [\rho_N] \right| \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle \\
&+ \left\langle \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^0 \left| \hat{v}_{\text{ext}}^0 [\rho_N] \right| \Psi_{\rho_{N-1}^\gamma}^0 \right\rangle + \left\langle \Psi_{\rho_{N-1}^\gamma}^0 \left| \hat{v}_{\text{ext}}^0 [\rho_N] \right| \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^0 \right\rangle \\
&- \gamma \frac{\partial}{\partial \gamma} \left\langle \Psi_{\rho_{N-1}^\gamma}^0 \left| \hat{V}_{ee} \right| \Psi_{\rho_{N-1}^\gamma}^0 \right\rangle. \tag{A5}
\end{aligned}$$

This equation can be simplified since

$$\begin{aligned}
& \left\langle \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{v}_{\text{ext}}^\gamma [\rho_N] \right| \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle + \left\langle \Psi_{\rho_{N-1}^\gamma}^\gamma \left| \hat{v}_{\text{ext}}^\gamma [\rho_N] \right| \frac{\partial}{\partial \gamma} \Psi_{\rho_{N-1}^\gamma}^\gamma \right\rangle \\
&= \int d^3 r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} \hat{v}_{\text{ext}}^\gamma([\rho_N]; \mathbf{r}). \tag{A6}
\end{aligned}$$

Using^{16,17}

$$\begin{aligned}\left\langle \Psi_{\rho_{N-1}}^0 \left| \hat{V}_{ee} \right| \Psi_{\rho_{N-1}}^0 \right\rangle &= E_x [\rho_{N-1}^\gamma] + U [\rho_{N-1}^\gamma] \\ &= E_{hx} [\rho_{N-1}^\gamma],\end{aligned}\tag{A7}$$

where $E_{hx} [\rho_{N-1}^\gamma]$ the sum of the exchange $E_x [\rho_{N-1}^\gamma]$ and Hartree interaction energy $U [\rho_{N-1}^\gamma]$ of the $(N-1)$ -electron system and the charge density ρ_{N-1}^γ is a function of γ ¹⁶,

$$\frac{\partial}{\partial \gamma} \left\langle \Psi_{\rho_{N-1}}^0 \left| \hat{V}_{ee} \right| \Psi_{\rho_{N-1}}^0 \right\rangle = \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} v_{hx}([\rho_{N-1}^\gamma]; \mathbf{r}),\tag{A8}$$

where

$$v_{hx}([\rho_{N-1}^\gamma]; \mathbf{r}) = \frac{\delta}{\delta \rho_{N-1}^\gamma(\mathbf{r})} (E_x [\rho_{N-1}^\gamma] + U [\rho_{N-1}^\gamma])\tag{A9}$$

is the sum of the exchange and Hartree potentials for the $(N-1)$ -electron system. Using Eqs. (A6), (A8), (13) and the fact that $|\Psi_{\rho_{N-1}}^\gamma\rangle$ and $|\Psi_{\rho_{N-1}}^0\rangle$ yield the same density ρ_{N-1}^γ by construction, Eq. (A5) can be expressed as

$$\begin{aligned}& \frac{\partial}{\partial \gamma} E_c^\gamma [\rho_{N-1}^\gamma] \\ &= \frac{E_c^\gamma [\rho_{N-1}^\gamma] - T_c^\gamma [\rho_{N-1}^\gamma]}{\gamma} \\ &+ \int d^3r \frac{\partial \rho_{N-1}^\gamma(\mathbf{r})}{\partial \gamma} (v_c^\gamma([\rho_N]; \mathbf{r}) + \gamma v_{hx}([\rho_N]; \mathbf{r}) - \gamma v_{hx}([\rho_{N-1}^\gamma]; \mathbf{r}))\end{aligned}\tag{A10}$$

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